(NASA CR-53299; GER-11318 S2) OTS: ---

CODE IDENT NO. 25500

GOODYEAR AEROSPACE CORPORATION

② Space Systems Div.

AKRON 15, OHIO

1. RIGIDIZED INFLATABLE

SOLAR ENERGY CONCENTRATORS

By

N. Jouriles and ~~Dr.~~ C. E. Welling 23 Jan. 1964 11p refs

Third Monthly Progress Report

Covering Period From 1 December ~~Through~~ 31 December 1963

(NASA Contract ~~No.~~ NAS1-3301) Control No. L-2923

January 23, 1964

LIBRARY COPY

JAN 29 19..

LANGLEY RESEARCH CENTER
LIBRARY, NASA
LANGLEY ST...
HAMP...

Prepared For

NASA Langley Research Center
Langley Station
Hampton, Virginia

By

② Space Systems Division
Goodyear Aerospace Corporation
1210 Massillon Road
Akron 15, Ohio

218-52 (5-63)
REF: ENGINEERING PROCEDURE 5.017

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

77.10 (5-63)
REF: ENGINEERING PROCEDURE S-017

17769

I. INTRODUCTION

This third monthly progress report covers the work accomplished from 1 December through 31 December 1963.

Up to now azide structures under investigation have been produced in the Goodyear Aerospace Corporation (GAC) laboratory. Structures I through IX (see Table I) have been under development with the greatest success being obtained with Structure I. On the basis of past development efforts (conducted under GAC R&D programs) three new azide structures were designed and ordered - during the first month of this contract. Small quantities of these structures have been delivered and are undergoing formulation and screening tests to determine their suitability for the ultimate objective. In addition to the azides, some new polyol resins were obtained for their desirable heat of distortion properties, and will be used in combination with the azides to produce an improved rigidizing material.

Trial runs were made on several new combinations. A number of experimental foams were produced by heat triggering in partially evacuated environments. The technique of determining the "Heat of Decomposition" has been developed and tests have been run on several structures where measurements show good relative consistency. An azotometer has been assembled and the nitrogen release has been determined for several azide structures. An apparatus has been built to determine the sublimation tendency of the azide-polyol combination in vacuum and at temperature. A "Vicat Softening Point" apparatus is being investigated for screening tests.

AUTHOR

77.10 (5-63)
REF: ENGINEERING PROCEDURE S-017

II. WORK ACCOMPLISHED DURING THIS REPORTING PERIOD

A. Azide Synthesis

A 22-gram quantity of terephthaloyl azide (Structure I) was synthesized in order to have a fresh material to compare with material synthesized more than 6 months ago. It is known that this azide is slightly unstable at room temperature, undergoing decomposition at a rate of the order of one per cent per month. We observe the fresh material to be more sensitive to heat induced detonation than the old, and note change in color from white to yellow in the old material that occurred on exposure to light for a few days. Color stability of the new material, which is being stored in the dark in a refrigerator, is so far good. Further determination of changes with aging may be made as time permits.

Delivery was made by our supplier of 25-gram quantities of azide Structures X and XI in apparently good condition and purity. Preliminary values for density, melting point, rate of decomposition at one temperature, and comments on explosive sensitivity are contained in Table I for Structures X and XI together with like information for Structure I. At this point it appears X and XI have as suitable thermal decomposition characteristics as I and somewhat less explosive potential. Further evaluations and comparisons must of course be made. A preliminary sample from attempts to synthesize Structure XII was received; its true molecular structure is however uncertain and it contains at least one impurity, according to the supplier. All structures, on preliminary tests, have shown similar polymerization reaction rates in foaming.

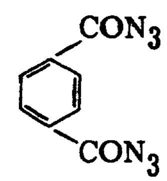
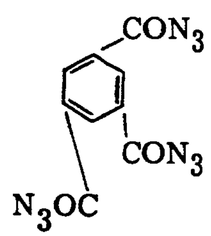
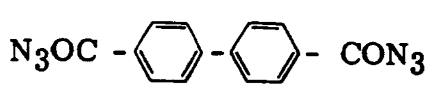
Infrared spectrophotometric inspections of the new azides will be made and it is planned to make inspections for purity by thin layer chromatography when equipment becomes available.

B. Foaming Studies

Experiments have been made with the objective of producing foamed specimens within molds under vacuum. In earlier work vacuum foaming was done with radiant heat directed downwards onto approximately six-inch diameter specimens of aluminized Mylar film carrying a coating, on the upper (clear) side, of the azide-resin mixture. The present work was done by placing a charged mold inside a vacuum dessicator that was heated within a laboratory oven. Foaming times of several hours at oven temperatures around 170 F were employed with formulations of Structure I and a partial prepolymer of PFR-6 resin. Under these conditions no violent exotherms occur. However, satisfactory cell structure within the 1 x 1 x 5 inch cavity was not obtained. The prolonged foaming period allows too much time for coolescence of small bubbles and gravity drainage; disproportionately heavy skins also form against cavity walls.

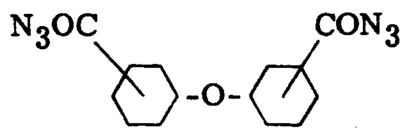
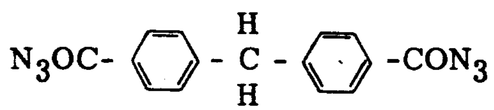
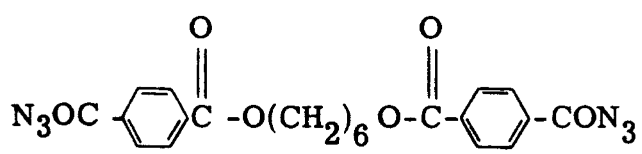
77.10 (5-63) REF: ENGINEERING PROCEDURE 5.017

Table I. Properties of Acid Azides

Structure	Azide Name and Mol Structure	Azide Function-ality	Isocyanate Produced on Re-arrangement	Azide N Content (Wt %) Total	Azide N Content (Wt %) Releasable	Azide Melting Point (°F)	Crystal Density of Azide (g/cc)	Half Life** at Stated Temperature (min)	Heat Release on Rearrangement at 275°F (cal/g)	Remarks Pertaining to Azides
I*	Terephthaloyl Azide  Mol wt = 216	2	1, 4-Benzene Diisocyanate Mol wt = 160 Amine eq = 80	38.9	25.9	230 - 232	1.58	30 - 40 (prelim) at 196°F	282	Shock sensitive. Heat sensitive. ~one percent/ month decom-position at 70°F.
II*	Mesoyl (tri) Azide  Mol wt = 285	3	1, 3, 5-Benzene Triisocyanate Mol wt = 201 Amine eq = 67	44.2	29.5	174	--	--	--	Extremely shock sensitive.
III*	Sebacoyl Azide $N_3OC\ (CH_2)_8CON_3$ Mol wt = 252	2	Octamethylene Diisocyanate Mol wt = 196 Amine eq = 98	33.3	22.2	~75 (litera-ture value 93)	--	--	--	Noticeably thermally un-stable at 75°F.
IV*	4, 4'-Diphenoyl Azide  Mol wt = 292	2	4, 4'-Biphe-nylene Diisocyanate Mol wt = 236 Amine eq = 118	29.8	19.2	259	--	--	--	Perhaps too thermally stable. Di-isocyanate is a known carcinogen.

*First synthesized and studied on Goodyear Aerospace in-house development program.
**Assuming a unimolecular reaction, the time for 50 percent of the material to undergo rearrangement as measured by nitrogen release.

Table I. Properties of Acid Azides (Continued)

Structure	Azide Name and Mol Structure	Azide Function-ality	Isocyanate Produced on Re-arrangement	Azide N Content (Wt %)		Azide Melting Point (^{o}F)	Crystal Density of Azide (g/cc)	Half Life** at Stated Temperature (min)	Heat Release on Rearrangement at 275^{o}F (cal/g)	Remarks Pertaining to Azides
				Total	Releasable					
IX†	Di-Acyl Azide of Oxy-Dibenzoic Acid  Mol wt = 308	--	--	27.3	18.2	--	--	--	--	--
X	4,4' -Diphenyl Methane Diacyl Azide  Mol wt = 306	2	4,4' -Diphenyl Methane Diisocyanate Mol wt = 250 Amine eq = 125	27.4	18.3	--	1.34	30 (prelim) at 193^{o}F	--	Have not observed detonation on rapid heating.
XI	 Mol wt = 464	2	-- Mol wt = 408 Amine eq = 204	18.1	12.1	--	1.31	30 (prelim) at 196^{o}F	--	Have not observed detonation on rapid heating.

**Assuming a unimolecular reaction, the time for 50 percent of the material to undergo rearrangement as measured by nitrogen release.
† Preparation of this structure contemplated during the Goodyear Aerospace in-house development program.

In view of the above problem, continuing tests of the utility of silicone polymers for stabilizing froths are being made. Some difficulties either with retarded cure or foam plasticization have been encountered. Silicone surfactants capable of stabilizing mechanically produced froths at room temperature seem ineffective at 175° F.

C. Measurement of Azide Thermal Decomposition Rates

An azotometer (similar to a nitrometer) apparatus was used to measure the volume of nitrogen evolved during the rearrangement of an azide material. The rate of azide decomposition is directly related to the rate of nitrogen evolved. Azotometer information gives the rate and amount of nitrogen evolved when the azide is exposed to a specific temperature. From these runs a value "K" for the reaction velocity of azide rearrangement can be arrived at. Then from the expression below the rate of azide decomposition can be determined for any time period.

$$\frac{dx}{dt} = -kx$$

where x = amount of azide
t = time after start of azotometer run
k = reaction velocity of azide rearrangment

D. Determination of Sublimation Tendency

An apparatus was constructed of a copper plate with a number of wells for copper cups which would contain the sample materials. A heating element is mounted on the underside of this plate for temperature control and thermocouples are mounted on the surface for temperature readings. This apparatus is contained in a belljar where temperature and pressure may be controlled.

The sublimation tendency of the candidate predistributed rigidizing materials is being determined by the weight loss method. Formulations of the material are prepared and applied to the caps of the apparatus described above. The caps then are subjected to a high vacuum environment for a specified time interval after which one cup is removed and the weight loss determined. With a minimum exposure to the atmosphere, the remaining cups are returned to the high vacuum environment. After a specified time exposure, a second cup is removed and the weight loss determined. This procedure continues until a curve can be established for the rate of sublimation of the material.

77.10 (5-63) REF: ENGINEERING PROCEDURE 5.017

III. PROBLEM AREAS

As reported in the preceeding monthly progress report (GER-11318 S1) the time required to locate an azide supplier, and the time required for the preparation and delivery of the first azide structure, have delayed the completion of Phase I of this program. This delay, however, is not expected to affect the completion date of the program.

IV. WORK TO BE PERFORMED DURING THE NEXT REPORTING PERIOD

A. The measurement of chemical and physical properties of all available azides will be continued.

B. Work will be continued to study formulation variations and their effect upon polymer strength and temperature dependence of strength. A Vicat softening apparatus will be employed to aid in these investigations.

C. Evaluation methods for azides will be continued. The areas of investigation will include:

1. Determination of shock sensitivity (and friction sensitivity).

2. Thermal decomposition characteristics of all available azides time versus temperature.

3. Heat release on decomposition as determined by calorimetry will be completed for all available azides.

4. Solubility in solvents and in prepolymer.

5. Sublimation tendency in high vacuum.

6. Test formulations made with consideration of:

   a. Balance between -OH and produced -NCO.

   b. Available releasable nitrogen for blowing.

   c. Azide decomposition rate as determined by azotometer, urethane reaction rate and viscosity when blowing.

   The above are to be evaluated in terms of density, foam polymer melt temperature, heat effects, cell structure, post cure and distortion.

D. Some material screening will be exercised, and possibly some new azides may be designed.

77.10 (5-63)
REF: ENGINEERING PROCEDURE 5.017

FIGURE 1 EAP 3-1169

SCHEDULE - RIGIDIZED INFLATABLE SOLAR CONCENTRATOR INVESTIGATION